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(71) Applicant: SUD-CHEMIE, INC. [US/US]; 1230 South 13th Street, Louisville, KY 40210 (US).

(72) Inventor: ZODY, G. Mark,; 6601 Routt Road, Jeffersontown, KY 40299 (US).

(74) Agents: CLARK, W., Robinson, H. et al.; Dorsey & Whitney LLP, Suite 300 South, 1001 Pennsylvania Avenue, N.W., Washington, DC 20004 (US).

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(54) Title: NONIONIC ASSOCIATIVE THICKENER COMPOSITION WITH IMPROVED VISCOSITY RETENTION UPON TINTING IN ARCHITECTURAL LATEX COATING

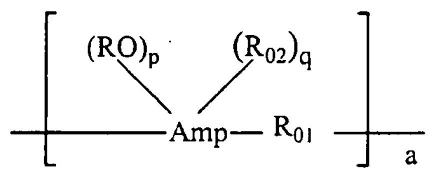
(57) Abstract: The present invention relates to a latex coating composition that contains at least one linear aminoplast ether copolymer having a relatively high hydrophobe content and sufficient to thicken the latex coating without the need for additional thickeners.

NONIONIC ASSOCIATIVE THICKENER COMPOSITION WITH IMPROVED VISCOSITY RETENTION UPON TINTING IN ARCHITECTURAL LATEX COATING

BACKGROUND TO THE INVENTION

1. Technical Field

The present invention relates to a water soluble copolymer composition containing a linear aminoplast-ether copolymer possessing a relatively high content of the hydrophobe tristyryl phenol. Such a copolymer contains a unit of the formula:



wherein the divalent R_{01} contains a divalent alkyleneoxy containing moiety, Amp is the skeletal residue of an aminoplast, as stated above, R is hydrogen, alkyl containing 1 to about 4 carbon atoms, or acyl containing 1 to about 4 carbon atoms, RO is bonded to alkylene units of Amp, and a is a number greater than 1, preferably greater than 2. Amp includes any dimer and oligomer component of the aminoplast. R_{02} is tristyryl phenol, that is covalently bonded to Amp through a heteroatom, p_2 is number that is equal to the free valence of Amp minus (2 + q), and q is a positive number

2. Background

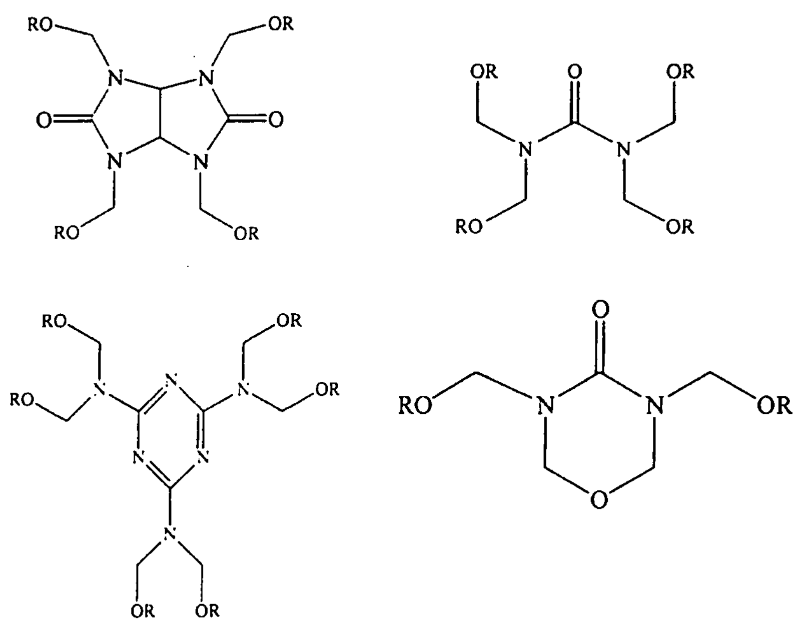
Nonionic associative thickeners have been used in latex architectural coatings for nearly 20 years. They have replaced the traditional cellulosic thickeners because coatings that utilize nonionic associative thickeners exhibit improved application properties such as brush drag, flow and leveling, and water sensitivity. The term "associative thickener" is recognized in the art to mean a nonionic hydrophobically modified water-soluble polymer capable of interacting in aqueous solution with itself and with other species such as latex particles. Associative thickeners are widely used to enhance the performance properties of paints and coatings. The use of associative thickeners in water based compositions are described in a

number of patents, including U.S. Patent Nos. 5,574,127, 4,426,485, 4,155,892, 4,079,028; 3,035,004; 2,795,564; 2,875,166 and 3,037,952.

One type of associative thickener is described by the two Emmons et al. patents, U.S. Pat. No. 4,079,028 and U.S. Pat. No. 4,155,892, patented Mar. 14, 1978 and May 22, 1979, respectively. These patents describe polyurethane associative thickeners that contain hydrophobic groups interconnected by hydrophilic polyether groups. The thickeners are nonionic.

Another type of associative thickener is described in US Patent Nos. 5,627,232 and 5,629,373 issued on May 6, 1997 and May 13, 1997 respectively. These patents describe water-based coating compositions containing a water soluble linear aminoplast-ether copolymer containing aminoplast segments interlinked through ether segments. Aminoplasts are defined in those patents, and herein, and in the claims, as an A-stage class of thermosetting resin based on the reaction of an amine with an aldehyde and the related acetals containing amines or amides. The structural features and commercial uses of aminoplasts are also described in detail in those patents. Figure 1 contains a partial list of aminoplasts.

Fig 1.



US Patent Nos.5,627,232 and 5,629,373 describes a linear aminoplast-ether copolymer with the formula as described in Fig 2.

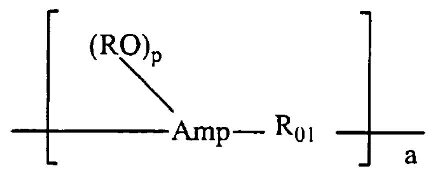


Fig 2.

where the divalent R_{01} contains a divalent alkyleneoxy containing moiety, Amp is the skeletal residue of an aminoplast, R is hydrogen, alkyl containing 1 to about 4 carbon atoms, or acyl containing 1 to about 4 carbon atoms, p is a positive number that is equal to the free valence of Amp minus 2, RO is bonded to alkylene units of Amp, and a is a number greater than 1.

For the purposes of this invention and the discussion of the prior art, the skeletal unit of the aminoplast is the structure of the aminoplast minus the RO— leaving groups bonded to alkylene of the alkylol or alkylol ether or ester of the aminoplast, regardless of whether any of the RO— groups are removed from the aminoplast. That skeletal unit is referred to herein and in the claims as "Amp."

The term "linear," when used herein and in the claims to characterize a polymer, relates to a polymer that is devoid of crosslinking or branching that renders the polymer solid and cured. A "wholly linear" polymer is a polymer that is devoid of crosslinking and branching. A linear polymer may or may not be a wholly linear polymer.

The term "acrylic polymer" means any polymer wherein at least 50% by weight is an acrylic or methacrylic acid or ester, including mixtures of such acids and esters individually and together. The term "vinyl acetate polymer" means any polymer containing at least 50% by weight of vinyl acetate.

The symbols and designations used herein are intended to be consistently applied, especially as used in formulations and equations, unless specifically stated otherwise. Typical nonionic associative thickeners have had only limited success when used in latex coatings for the mid to neutral base

formulations based on small particle size acrylics. The problem arises when colorants are added to said formulations. The addition of colorant in the amounts of about 5 ounces or above results in a substantial reduction in the viscosity of the coating. This reduction in viscosity leads to undesirable coating properties and has been addressed by architectural coating manufacturers in a number of ways.

One method manufacturers have used is to compensate for the viscosity drop that occurs upon tinting. The coating is formulated to have a very high viscosity before the colorant is added. The colorant is added expecting that the viscosity of the coating drop to an acceptable level. Another method that manufacturers have used is to incorporate large amounts of surfactants and solvents into the coating to control the viscosity drop upon tinting. Still yet another method used by manufacturers is to incorporate other thickening agents such as cellulosics and alkai-swellable thickeners to compensate for the viscosity drop. While these methods do address the viscosity problem, each of these corrective methods has problems associated with them that make their use less than ideal.

The problem with formulating a pre-tinted coating with a very high viscosity is that it creates problems in the manufacturing process. The problem with additives such as surfactants and solvents, or cellulosics and alkai-swellable thickeners is that it compromises the application properties of the resulting coating. The additives can also cause problems with the physical properties of the final dried paint film. For example, high levels of surfactants or the use of alkai-swellable thickeners can lead to water sensitivity or poor scrub resistance

What is needed is a nonionic associative thickener that can be used in latex coatings for the mid to neutral base formulations based on small particle size acrylics that results in minimal reduction in viscosity when the colorant is added.

What is needed is a nonionic associative thickener that can be used in latex coatings of the mid to neutral base formulations based on small particle size acrylics that does not need the addition of surfactants and solvents, or other thickening agents to achieve a satisfactory viscosity when the colorant is added.

What is needed is a nonionic associative thickener that can be used in latex coatings for the mid to neutral base formulations based on small particle size acrylics that maintains desirable

application properties when the colorant is added without compromising the final film properties.

Summary of the Invention

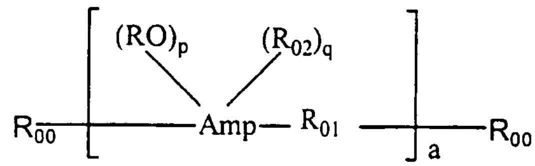
The present invention relates to a water soluble copolymer composition containing a linear aminoplast-ether copolymer possessing a relatively high content of the hydrophobe tristyryl phenol. Such a copolymer contains a unit of the formula:

$$\left[\overset{(RO)_p \diagdown \quad \diagup (R_{02})_q}{\text{———Amp— } R_{01}} \text{ —} \right]_a \qquad \text{I.}$$

wherein

the divalent R_{01} contains a divalent alkyleneoxy containing moiety, Amp is the skeletal residue of an aminoplast, as stated above, R is defined above, RO is bonded to alkylene units of Amp, and a is a number greater than 1, preferably greater than 2. Amp includes any dimer and oligomer component of the aminoplast. R_{02} is tristyryl phenol, that is covalently bonded to Amp through a heteroatom, p_2 is number that is equal to the free valence of Amp minus (2+ q), and q is a positive number. The relatively high content of the hydrophobe means a copolymer that contains more than about 3% tristyryl phenol based on weight. In the preferred embodiment, the copolymer contains about 4% tristyryl phenol to about 10% tristyryl phenol based on weight when the polymer is produced using polyethylene oxide and a glycoluril compound.

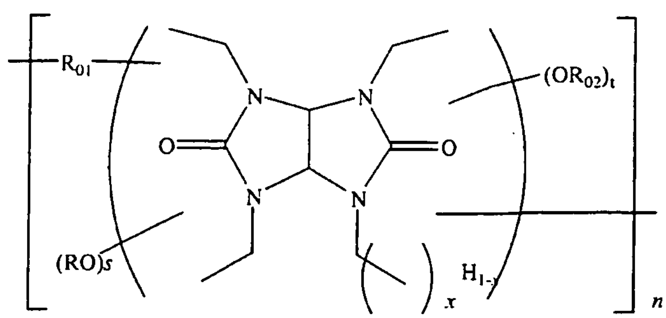
In another embodiment of the invention, the invention relates to a novel water-based coating composition that contains a linear aminoplast-ether copolymer possessing end groups characterized by a component of the units making up the copolymer, or a monofunctional group that effectively end-caps the copolymer, forming the end group. This yields a copolymer of the formula:



II.

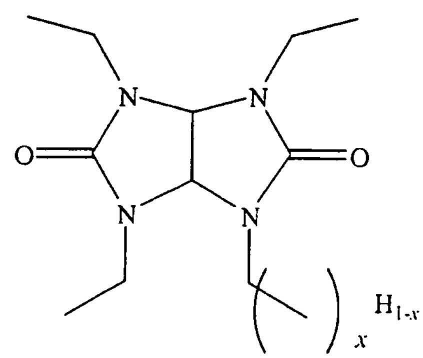
where each R_{00} is the same or different terminal group, such as hydrogen, —R_{01}—H, Amp bonded —$(OR)_{p1}$, —Amp—$(OR)_{p1}$, tristyryl phenol, or any other monofunctional organic groups, such as alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkyoxyalkyl, aroxyalkyl, cycloalkoxyalkyl, and the like, and p_1 is a positive number that is equal to the free valence of Amp minus 1

A particularly preferred linear aminoplast-ether copolymer comprises units of the formula:



III.

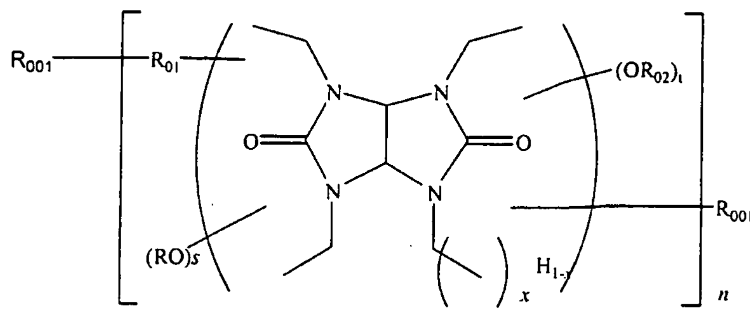
wherein R_{01}, R_{02}, and R are described above, n has a value of at least 2, x is 0 or 1, and s+t equals (i) the free valence of the



IV.

moiety and (ii) 4-x; and the average value of t/s+ t is about 0.01 to about 0.5.

In a further preferred embodiment of the invention, the linear aminoplast-ether copolymer employed in the coating composition of the invention comprises a copolymer that possesses end groups as illustrated by the following structure:



V.

wherein each R_{001} is the same or different terminal group, such as hydrogen, —R_{01}—H, —$(OR)_{p1}$, —Amp^0—$(OR)_{p1}$, tristyryl phenol, or any other monofunctional organic groups, such as alkyl, cycloalkyl, aryl, alkaryl, aralkyl, alkyoxyalkyl, aroxyalkyl, cycloalkoxyalkyl, and the like, and p_1 is a positive number that is equal to the free valence of Amp^0 minus 1. Amp^0 is depicted in formula V.

The present invention further relates to a latex coating for the mid to neutral base formulations based on small particle size acrylics. The present invention improves on this type of latex coatings by reducing the drop in viscosity that normally occurs when the colorant is added to latex coating for the mid to neutral base formulations based on small particle size acrylics. The present invention also yields overall improved color acceptance compared to other compositions and competitive products.

Detailed description of the invention

This invention relates to the use of any aminoplast, including those specifically recited in FIG. 1 above, to make the copolymer of the invention. Of these aminoplasts, exceptional performing associative

thickeners, for use in latex coatings for the mid to neutral base formulations based on small particle size acrylics, are obtained from the reaction of glycolurils with alkylene oxide glycols to which are incorporated the tristyryl phenol pendant moieties.

The linear aminoplast-ether copolymers of formula I et seq. are made by the novel condensation reaction of a polyfunctional aminoplast with a di-functional polyether (alone or with another polyol, as characterized with respect to formulae XII and XIII) in the presence of an acid catalyst. In the prior art, as noted above, aminoplasts are condensed with polyfunctional compounds to produce thermosetting resins or thermoset products (i.e., C-stage resin). This reaction produces a linear copolymer. Thus, the copolymers of formulae I, II, III, IV, and V are either liquid or thermoplastic solids that are solvent soluble and water soluble or dispersible.

The linear aminoplast-ether copolymer are made by the copolymerization reaction of a polyfunctional aminoplast with an ether containing two active hydrogen terminal groups, in the presence of an acid catalyst, especially a Brönsted-Lowery acid provided in catalytically effective amounts. The reaction is continued until the desired molecular weight is achieved. The desired molecular weight of the copolymer is dependent on the intended use of the copolymer. The molecular weight of the copolymer may range from about 12,000 to about 800,000, preferably from about 20,000 to about 100,000, and most preferably from about 30,000 to about 80,000. The aminoplast is a polymerizable resin of the general formula:

$$(RO)_{\overline{z}}\!\!-\!\!\!-\!\!\!-\mathrm{Amp} \qquad \mathrm{VI}$$

wherein z is a positive number having a value of at least **2.** The ether containing two active hydrogen terminal groups comprises a wide variety of compositions. A preferred class is nonionic. Illustrative of a preferred class of such ethers are polyalkylene oxides of the formula:

$$\mathrm{H}\text{— Alkylene Oxide —}\mathrm{H} \qquad \mathrm{VII.}$$

where "alkylene oxide" is a divalent moiety containing at least two alkylene oxide units in which

1. the alkylene oxide units form a linear chain and provide a terminal OH, or

2. the alkylene oxide units are bonded to a starter molecule, such as a diamine, urea, carbamate, phenoxy, amide, bis-imide, and the like, and providing a terminal OH, and/or

3. in which alkylene oxide are bonded to a terminal group that possesses a moiety that provides the active hydrogen (—H in formula VII).

Further illustrative of such a preferred class are the water soluble or dispersible polyether compounds of the formula:

$$H_{x1}X—(R_{04})_{x4}(R_{05})_{x5}(R_{06})_{x6}(R_{07})_{x7}(R_{08})_{x8}—XH_{x2} \qquad \text{VIII.}$$

wherein

X is an active hydrogen functional moiety such as oxy (—O—), sulfidyl (—S—), amino (—N<), carboxy (—COO—), carboxamido, silyl, phosphoryl, ureido, and the like;

R_{04} and R_{08} are alkyl of 2 to about 8 carbon atoms;

R_{05} and R_{07} are one or more alkylene oxide units, e.g., such as water soluble or dispersible ethylene oxide, propylene oxide, mixed ethylene oxide/1,2-propylene oxide, mixed ethylene oxide/1,3-propylene oxide, mixed ethylene oxide/1,2-butylene oxide, mixed ethylene oxide/1,4-butylene oxide, and the like;

R_{06} is a divalent group such as alkyleneoxy, alkylenepolyamine, cycloalkylene polyamine, phenoxy, uriedo, carbamate, amide, and the like;

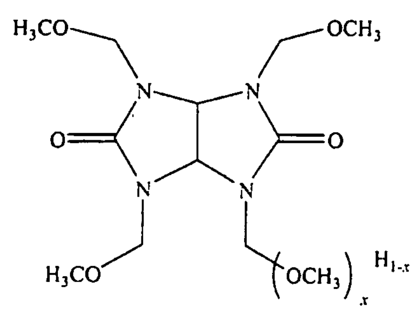
x1 and x2 are each equal to the free valence of X;

x3, x4, x5, x6 and x7 are each 0 or 1, and one or more of x4 and x6 is 1.

Specific illustrations of a limited class of polyethers encompassed by formula VIII are the Carbowax® and Pluracol® polyether diols sold by Union Carbide Chemicals & Plastics, Inc. and BASF Performance Chemicals, respectively. There are a variety of functional fluids based on alkylene oxides that are sold by Union Carbide Chemicals & Plastics, Inc. and BASF Performance Chemicals that are encompassed by formula VIII. The molecular weight of the polyether reagent may range from about 106 and lower, to about 35,000, and higher.

In the prior art, as noted above, aminoplasts are condensed with polyfunctional compounds to produce thermosetting resins or thermoset products (i.e., C-stage resin). The above method produces a linear copolymer. Thus, the copolymers of formulae I, II, III, IV, and V are either liquid or thermoplastic solids that are solvent soluble and water soluble or dispersible.

Aminoplast reagents include, but are not restricted to, aldehyde reaction products of melamines, ureas, benzoguanamines, glycolurils, and the like, to produce the array of aminoplasts, including but not limited to those described in FIG. 1 above. While any of these can be used to make associative thickeners, the glycolurils, such as those of formula IX



IX

where R and x are defined above, have shown appropriate hydrolyric stability, when reacted with the polyether compounds, such as those encompassed by formula VIII, to meet commercial criteria for associative thickener-containing coating compositions. However, the reaction products of such aminoplasts with, e.g., thiols and NH groups from amides and carbamates, encompassed by formula VIII, are much

more hydrolytically stable than aminoplast ether linkages. The use of such reactants allow for the production of most hydrolytically stable aminoplast-based copolymers.

Suitable polyethers include polyalkylene polyethers. The preferred polyethers are water soluble. The most preferred polyethers are the alkylene polyethers where the predominant alkylene groups are ethylene. The most desirable polyethers are polyethylene oxide diols that possess molecular weights from about 1,000 to about 35,000.

Illustrative of the desirable polyethylene oxide diols are those of the formula:

$$HO\text{—}(\text{—}CH_2CH_2O)_{x11}CH_2CH_2OH \qquad \text{X.}$$

wherein x11 has a value of about 20 to about 800, preferably from about 50 to about 500, and most preferably from about 100 to about 300.

A further desirable embodiment of the invention is the modification of the linear aminoplast-ether copolymers used in making the coatings of the invention by including a minor mole proportion of the following unit structure in the repeating structure of the copolymer:

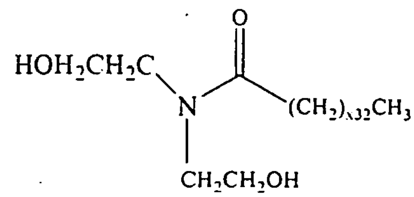
$$\text{—Amp—}R_{15}\text{—} \qquad \text{XI.}$$

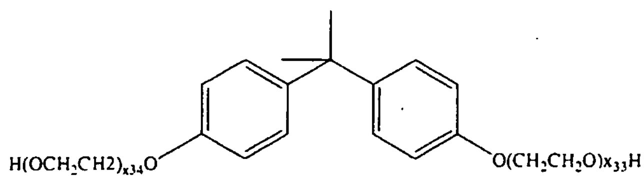
wherein R_{15} is the residue of a diol possessing greater hydrophobicity than R_{01}, thereby providing for a linear copolymer containing the structure

$$\text{—}\left[\text{Amp—}R_{01}\right]_{x29}\text{—} \quad \text{—}\left[\text{Amp—}R_{15}\right]_{x30}\text{—} \qquad \text{XII}$$

wherein x29 has a value that is greater than x30. Preferably, x30/x29 is less than about 1, preferably less than about 0.33. Illustrative of such R_{15} groups are

$$HO(CH_2)_{x31}OH$$





wherein x31 has a value of about 8 to about 20, x32 has a value of about 8 to about 23, x33 and x34 have values of 0 to about 8. The linear copolymer of formula XII may be modified to possess the terminal groups of formulae II and V, discussed above.

The linear aminoplast-ether copolymers of this invention, contains a hydrophobe pendant group. Acceptable hydrophobe groups include aliphatic to alkyl phenol to tristyryl phenol. The most preferred hydrophobic pendant group is tristyryl phenol. Tristyryl phenol extends from aminoplast component of the linear backbone of the aminoplast-ether copolymer. Tristyryl phenol groups are typically bonded to the backbone through ether or ester groups, as illustrated in formula II. The presence of tristyryl phenol enhances the performance of the resulting aminoplast-ether copolymer as an associative thickener in architectural coating compositions for the mid to neutral base formulations based on small particle size acrylics where the level of colorant added is in large amounts for about the 5 to 16 oz per gallon range.

This invention relates to the use of any aminoplast, including those specifically recited in FIG. 1 above, to make the copolymer of the invention. Of these aminoplasts, exceptional performing associative thickeners are obtained from the reaction of glycolurils with alkylene oxide glycols to which are incorporated tristyryl phenol pendant moieties at a relatively high concentration. The relatively high concentration of tristyryl phenol means about 3% or greater based on weight. In the preferred embodiment the concentration of tristyrl phenol is at a concentration of about 4% to about 10% based on weight.

The production of the aminoplast-ether copolymers are made by solvent or melt polymerization. The typical preparation of an aminoplast-, such as glycoluril-, based associative thickener involves dissolving the aminoplast (e.g., glycoluril), a polyether compounds within the scope of formula IX (such as a Carbowax® polyether sold by Union Carbide Chemical and Plastics, Inc., Danbury, Conn.), with or without the addition of a more hydrophobic polyol within the scope of formula XI,with the addition of ethoxylated tristyryl phenol (such as Soprophor BSU), in a stripping solvent, such as alkylated benzene (e.g., toluene or xylenes). Prior to the combination of these reagent, each may be dried by azeotropic distillation with toluene, xylenes, or a mixture of them, or by any other drying procedure. Total concentration of the reagents in the solvent may be maintained from about 10 to about 60 weight %. The temperature of the mixture may be brought to about 60°-140° C., preferably to about 80°-120° C. An acid catalyst, such as a sulfonic acid catalyst, is then added. The reaction mixture is placed under reduced pressure to bring about a steady distillation of the toluene/xylenes which azeotropes the alcohol byproduct that must be removed in order for the reaction to proceed. Fresh solvent is constantly added to maintain a constant level. The reaction is allowed to proceed until a given high viscosity is achieved as measured by Gardner bubble tubes or until viscosity increase ceases. Such viscosity increase indicates an increase in the molecular weight of the copolymer.

SPECIFIC ILLUSTRATION OF SOLVENT PROCESS

The following is an illustration of the sequential steps involved in preparing the aminoplast-ether copolymer.

1. Polyether polyol, ethoxylated tristyryl phenol, and azeotroping solvent (e.g., toluene) are added to an appropriately sized container that accommodates a heater, temperature reading device, a nitrogen inlet, and a Dean Stark water trap and condenser.

2. The mixture of step 1 is heated to reflux to dry the mixture by azeotropic distillation. When water removal ceases, the mixture is cooled to about 100° C., and the water trap is removed. A distillation column and receiving vessel are installed in the container.

3. Glycoluril (e.g., Powderlink 1174) is added and allowed to melt.

4. The catalyst is added and vacuum is applied. The pressure is reduced to a level that causes a steady distillation of solvent at about 100° C. The solvent is continually replenished from a pressure equalizing add funnel.

5. As the reaction proceeds, samples are removed and cooled to room temperature, and the Gardner bubble viscosity is measured.

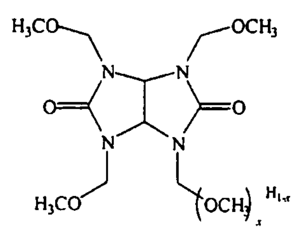
6. When the proper viscosity is reached, the heat is removed and the mixture is cooled in a water bath. When the temperature has been reduced to below 75° C., an amine neutralizing agent is added. When the temperature is reduced to below 65° C., the polymer solution is poured out onto trays to air dry.

7. The dried polymer is cut into strips and redissolved in water or water/cosolvent mixture.

Polymerization in the melt involves the admixture of the same reagents in the absence of a solvent with a heavy duty laboratory mixer (such as an Universal Sigma Blade Mixer, sold by Baker Perkins Guittard SA, Paris, France) at a temperature sufficient to generate leaving groups and remove the reaction condensation products. The removal of volatile byproducts by vacuum is necessary in order to shift the reaction to the right and prevent an equilibrium reaction from occurring that impedes the reaction before the desired degree of polymerization is achieved.

Catalysts useable for effecting the copolymerization reaction includes the standard Bröonsted-Lowery acid catalysts typically used for the condensation of aminoplast resins. Such acid catalysts include mineral acids (e.g., HCl, H_2SO_4, H_3PO_4, and the like), aryl sulfonic and alkylated aryl sulfonic acids, such as benzene sulfonic acid, p-toluene sulfonic acid, 1-naphthalene sulfonic acid, 2-naphthalene sulfonic acid, naphthalene-1,5-disulfonic acid, naphthalene-2,7-disulfonic acid, 1,3,6-naphthalene trisulfonic acid, naphtholsulfonic acid, dinonylnaphthalene disulfonic acid, dodecylbenzene sulfonic acid, oxalic acid, maleic acid, hexamic acid, alkyl phosphate ester, phthalic acid, and copolymerized acrylic acid. Of these catalysts, the sulfonic acid catalysts are the most effective and efficient for making the copolymers of the invention and dodecylbenzene sulfonic acid is the most preferred sulfonic acid catalyst.

Glycolurils are marketed by Cytec Industries as Cymel 1170, 1171, 1175 and Powderlink 1174. The Cymel versions are either mixed methylolated species and typically contain a relatively high dimer or oligomer content of up to about 20 weight percent. Powderlink 1174 is a purer form that is solely the methyl ester of the formula:



XIII

with about 3-5 weight percent of a dimer-oligomer of the monomer form. The purer the monomeric form of the aminoplast, the better it is in forming the copolymers of the invention. In about 5-7 weight percent of Powderlink 1174, x is 0, and such monomer form is trifunctional. The dimer-oligomer forms provide greater amounts of methoxy per molecule. For example, the dimer contains 6 methoxy functional groups. Such tri- and hexa-functionality does not alter this invention. The glycoluril ether linkage is much more resistant to hydrolysis than other aminoplast ether bonds. The higher dimer-oligomer content of the less pure

glycolurils is not as favored as the lower dimer-oligomer content of Powder link 1174.[1] Further reduction of oligomers can be effected by recrystallization.

[1]Powderlink 1174 is called a "resin" and "crosslinker" by Cytec, and has been sold under the Cymel® name (i.e., Cymel 1174). Its empirical structure is $C_{12}H_{22}N_4O_6$. Its chemical name is Imidazo [4,5-D] imidazole-2,5 (1H,3H)-dione, tetrahydro-1,3,4,6-tetrakis (methoxymethyl)-. CAS 17464-88-9. It is also known by the following names: (i) Glycoluril, 1,3,4,6 tetrakis methoxymethyl, (ii) Glycoluril, tetrakis methoxymethyl, (iii) Glycoluril, N,N,N,N tetrakis methoxymethyl, (iv) Glyoxal diuriene, tetrakis methoxymethyl, and (v) Tetramethoxytetramethylol acetylenediurea. The favored name is (i) and such skeletal structure is called glycoluril.

The ratio of aminoplast resin to the difunctional polyether is not critical. Typically, either the aminoplast resin or the difunctional polyether may be used in molar excess or stoichiometrically equivalent amounts in making the linear copolymer of the invention. In characterizing stoichiometry of the aminoplast resin, the resin is treated as being difunctional since linearity, according to the invention, is achieved when the aminoplast resin functions as a difunctional monomer even though the resin has the capability of higher functionality, e.g., tri- and tetrafunctionality, as the case may be. Thus, more than one mole of a polyether diol to one mole of, e.g., a glycoluril such as Powderlink 1174, represents a stoichiometric excess of the polyether to the glycoluril. Using this characterization, one may use between 1-2 moles of one of these reagents to 1 mole of the other. Either the polyether or the aminoplast may be in excess. However, it is more typical to use a mole amount of one reagent of about 1-1.75 to 1 of the other reagent. Typically, one employs a molar excess of the aminoplast resin because one may incorporate more hydrophobicity into the copolymer this way. This is especially the case when the copolymer is dimeric to oligomeric (e.g., possessing less than about 15 repeating units). When making higher polymeric structures, one uses a greater proportion of the polyether reagent, up to a 1:1 mole ratio. In general, it is desirable to use a molar excess of aminoplast of about 1.001-2.0 moles to 1 mole of the difunctional polyether. The amount of ethoxylated tristyryl phenol should not exceed about 2.0 moles, nor be less than about 0.4 mole per mole of reacted

aminoplast resin in the copolymer of the invention. Usually, the amount of ethoxylated tristyryl phenol ranges from about 0.7 mole to about 1.5 mole per mole of reacted aminoplast.

Waterborne coatings may be defined as coatings that contain water as the major volatile component and utilize water to dilute the coating to application consistency. These coatings consist mainly of resinous binder, pigments, water, and organic solvent. The type of pigmentation and the method of incorporation of the pigment vary widely.

Waterborne coatings can be made by dispersing, emulsifying or emulsion polymerizing the resin binder by use of added surfactants. This technique leads to opaque liquids. Because some hard resins are difficult or impossible to disperse directly into water, the resin sometimes can be dissolved in a water-immiscible solvent, and the resulting solution dispersed by the use of added surfactants. In this case, the solvent aids subsequent film coalescence. Surface activity or water dispersability also can be introduced into resin molecules by chemical modification of the resin by introducing functional polar groups such as the carboxyl group.

Some very finely dispersed resins appear as clear or slightly hazy liquids; they frequently are described as soluble, solubilized, colloidal dispersions, micro-emulsions, hydrosols, etc. These resins contain built-in functional groups that confer water "solubility" upon the resin, and, normally, external added surfactants are not used.

Waterborne resin binders can be classified as anionic, cationic, or non-ionic. Anionic dispersions are characterized by negative charges on the resin or by negative charges on the surfactant associated with the resin. Cationic dispersions have a positive charge on the resin or on the surfactant associated with the resin. Nonionic dispersions are those that have been dispersed by addition of nonionic surfactants or that contain a built-in hydrophilic segment such as polyethylene oxide which is part of the main chain of a relatively hydrophobic resin molecule.

The coating compositions may be of the thermosetting or thermoplastic varieties. The resin used in forming the coating may be insoluble in water, and the conversion of such a resin into a waterborne

system typically involves converting the resin into an emulsion or dispersion. In the context of this invention, the waterborne composition contains the aminoplast-ether copolymer associative thickener of the invention.

The aqueous polymer dispersions may be prepared according to well known emulsion polymerization procedures, using one or more emulsifiers of an anionic, cationic, or nonionic type. Mixtures of two or more non-neutralizing emulsifiers regardless of type may be used. The amount of emulsifier may range from about 0.1 to 10% by weight or sometimes even more, based on the weight of the total monomer charge. In general, the molecular weight of these emulsion polymers is high, e.g., from about 100,000 to 10,000,000 number average molecular weight, most commonly above 500,000.

The water insoluble resin may be any of those known in the art, and may be a conventional natural or synthetic polymer latex emulsified with one of a nonionic, cationic or anionic surfactant. The primary resins are based on homopolymerized and copolymerized olefinic monomers such as vinyl acetate; vinyl chloride; styrene; butadiene; vinylidene chloride; acrylonitrile; methacrylonitrile; acrylic acid; methacrylic acid; alkyl acrylates; alkyl methacrylates; acrylamide; methacrylamide; hydroxyethyl methacrylate ("HEMA"); glycidyl methacrylate; dihydroxypropyl methacrylate; homopolymers of C_2-C_{40} alpha-olefins such as ethylene, isobutylene, octene, nonene, and styrene, and the like; copolymers of one or more of these hydrocarbons with one or more esters, nitriles or amides of acrylic acid or of methacrylic acid or with vinyl esters, such as vinyl acetate and vinyl chloride, or with vinylidene chloride; and diene polymers, such as copolymers of butadiene with one or more of styrene, vinyl toluene, acrylonitrile, methacrylonitrile, and esters of acrylic acid or methacrylic acid, and the like. It is also quite common to include a small amount, such as 0.1 to 5% or more, of an acid monomer in the monomer mixture used for making the copolymers mentioned above by emulsion polymerization. Acids used include acrylic, methacrylic, itaconic, crotonic, maleic, fumaric, and the like.

The vinyl acetate copolymers are well-known and include copolymers such as vinyl acetate/butyl acrylate/2-ethylhexyl acrylate, vinyl acetate/butyl maleate, vinyl acetate/ethylene, vinyl acetate/vinyl chloride/butyl acrylate and vinyl acetate/vinyl chloride/ethylene.

Other waterborne systems involve reactive copolymers that are crosslinked by the presence of complementary functional groups in the system. For example, a copolymer of acrylic ester/glycidylmethacrylate can be emulsified and crosslinked by the presence of a melamine-formaldehyde resin similarly emulsified in the system. In another system, a copolymer of HEMA and another acrylate, hydroxyl terminated polyesters, polyethers, or polyurethanes, can be emulsified and crosslinked by the presence of either an aminoplast resin, a polyisocyanate or blocked polyisocyanate.

The term "acrylic polymer" means any polymer wherein at least 50% by weight is an acrylic or methacrylic acid or ester, including mixtures of such acids and esters individually and together. The term "vinyl acetate polymer" means any polymer containing at least 50% by weight of vinyl acetate.

Small particle size (about 0.1-0.15 micron) acrylic and other latices are thickened effectively, and flow and leveling improved, by thickeners of the invention. The use of this invention for producing architectural coatings for the mid to neutral base formulations based on small particle size acrylics where the level of colorant added is in large amounts for about the 5 to 16 oz per gallon range eliminates the need to incorporate other thickener systems, such as cellulosics and alkai-swellable thickeners or large amounts of surfactants.

The amount of the aminoplast-ether copolymer described herein that is employed in the coating composition of the invention is not critical. That amount will vary based on the resin system used, the water concentration, the amount of fillers and the choice of fillers, the presence or absence of thixotropic agents, and the like. In that respect, the amount of the aminoplast-ether copolymer in the composition is sufficient to thicken the composition. However, in general, the amount of the copolymer will range from about 0.1 weight percent to about 15 weight percent, preferably from about 0.5 weight percent to about 10 weight percent, and most preferably from about 1 weight percent to about 8 weight percent, of the weight of the coating composition, exclusive of fillers, pigments and like additives.

The following is an illustrative formulation for an architectural coating based on small particle size acrylic. Optiflo H600 is the aminoplast-ether copolymer described above.

EXAMPLE

1) Water, propylene glycol, Tamol 731, foamaster VL, Kathon LX are added to a high speed disperser tank equipped with a cowls high speed agitator blade. Agitation is begun followed by the addition of the R-900 dry TiO2 pigment. The mixture is ground at high speed (~2,000 rpm) for 20 to 30 minutes or until the TiO2 is well dispersed (usually determined using a hegman grind gauge of greater than 6).

2) Once the grind is complete the speed or shear is decreased and the grind paste is transferred to another tank equipped with a mixing blade (usually a slow speed paddle blade). The SG-10M and OP62 are added and mixed for approximately 10 minutes. The remaining ingredients can be added (water, Optiflo L100 and Optiflo H600). A defoamer (Foamaster VL) is usually added so as to remove any entrained air.

3) Quality Control checks usually consist of viscosity (Stormer & ICI), pH, weight per gallon (WPG), hiding power and color acceptance.

SEMI-GLOSS
SG-10M

GRIND		POUNDS	GALLONS
WATER		11.13	1.34
PROPYLENE GLYCOL		65.00	7.51
TAMOL 731		12.88	1.40
FOAMASTER VL		1.00	0.13
KATHON LX		1.80	0.22
TI-PURE R-900		253.00	7.60
	GRIND TiO2 @ 1300 rpm FOR 30 MINUTES RECORD MAXIMUM GRIND TEMPERATURE:		
LET DOWN	5 GALLON PAIL - 3F BLADE		

WATER	88	10.56
RHOPLEX SG-10	465.5	52.78
ROPAQUE OP-62	27.96	3.25
TEXANOL	24.32	3.07
SUB TOTAL:		
	950.62	87.87
MIX AT LOW SPEED 30 MINUTES		
RECORD WPG : 10.82		
RECORD pH:		
PREMIX:		
WATER	72.20	8.67
L100	28.35	3.28
H600	0.50	0.06
FOAMASTER VL	1.00	0.13
TOTAL:		
	1,052.67	100.00
	PVC%:	27.26
	VS%:	34.10

Paint Examples

Evaluation in a Neutral Base Latex Paint Formuation:

The 17.5% solution from example 1 was evaluated in a semi-gloss neutral base formuation which contained Rhopex SG-10M acrylic latex. The paints were tinted with 12 oz of F Colorant (red iron oxide) from CreaNova (888).

	Loading (Dry lbs/100gal)	Initial Stormer (KU)	Stormer after tinting (KU)	•KU
Example 1	0.525	108	98	10
Acrysol RM825	0.525	102	82	20

Evaluation in a deep Base Latex Paint Formulation:

The 17.5% solution from example 1 was evaluated in a semi-gloss neutral base formulation which contained Rhopex SG-20M acrylic latex. The paints were tinted with 8 oz of F Colorant (red iron oxide) from CreaNova (888).

	Loading (Dry lbs/100gal)	Initial Stormer (KU)	Stormer after tinting (KU)	●KU
Example 1	0.44	111	91	20
Acrysol RM825	0.44	110	64	246

We claim:

1. A latex coating based on small particle size acrylics with improved viscosity retention, comprising:

a) at least one pigment, water,

b) at least one dispersant,

c) at least one defoamer,

d) at least one aminoplast ether copolymer sufficient to thicken the latex coating without the need for additional non-aminoplast ether copolymer thickeners.

2. The latex coating of claim 1, wherein the aminoplast ether copolymer has a relatively high hydrophobe content.

3. The latex coating of claim of claim 2, wherein the hydrophobe content is about 3 to about 10% weight content.

4. The latex coating of claim of claim 2, wherein the hydrophobe is tristyryl phenol.

5. The latex coating of claim 2, wherein the amount of aminoplast ether copolymer is from about 0.1 weight percent to about 15 weight percent.

6. The latex coating of claim 2, wherein the aminoplast ether copolymer has a molecular weight of about 12,000 to about 800,000.

7. The latex coating of claim 5, wherein the hydrophobe is tristyryl phenol.

8. A method for making a latex coating with improved viscosity retention having the following steps:

(a) admixing water, a dispersant, a defoamer, propylene glycol, **and Kathon LX**;

(b) admixing in additional desired additives and pigments;

(c) **adding a premix** to the container; and

(d) optionally adding a defoamer to remove entrained air.

9. The method for making a latex coating of claim 8, wherein the premix comprises water and aminoplast ether copolymer.

10. The method for making a latex coating of claim 9, wherein the aminoplast ether copolymer contains a relatively high hydrophobe content.

11. The method for making a latex coating of claim 9, wherein the hydrophobe is tristyryl phenol.

12. The method of making a latex coating of claim 9, wherein the hydrophobe content is greater than about 3% by weight.

13. The method for making a latex coating of claim 8, wherein the dispersant comprises Tamol 731.

14. The method for making a latex coating of claim 8, wherein the defoamer comprises foamaster VL.

15. The method for making a latex coating of claim 8, wherein the pigments comprise TiO_2.

16. The method of making a latex coating of claim 9, wherein the aminoplast ether copolymer contains a relatively high hydrophobe content.

17 The method of making a latex coating of claim 16, wherein the hydrophobe is aliphatic, alkyl phenol, tristyryl phenol, or combinations thereof.

18. A method for making a small particle size acrylic latex coating with an improved viscosity retention having the following steps:

(a) admixing water, a <u>dispersant</u>, a <u>defoamer</u>, propylene glycol, **and Kathon LX**;

(b) admixing in additional desired additives and pigments;

(c) adding a <u>premix</u> to the container; and

(d) optionally adding a defoamer to remove entrained air.

19. The method for making a small particle size acrylic latex coating of claim 18, wherein the premix comprises water, Optiflo L100, and Optiflo H600.

20. The method for making a small particle size acrylic latex coating of claim 18, wherein the pigments comprise TiO_2.

21. The method for making a small particle size acrylic latex coating of claim 19, wherein the pigments comprise TiO_2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/22220

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.
US CL : US CL :524/388, 512, 593
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : US CL :524/388, 512, 593

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,289,811 A (SHELLEY, JR.) 15 September 1981, see columns 3-6.	1-21
X	US 5,627,232 A (GLANCY et al) 06 May 1997, see columns 4-19.	1-21
X	US 5,629,373 A (GLANCY et al) 13 May 1997, see columns 1-20.	1-21
X	US 5,914,373 A (GLANCY et al) 22 June 1999, see columns 4-21.	1-21
A,E	US 6,103,816 A (SWARUP et al) 15 August 2000, see columns 2-6.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 NOVEMBER 2000	13 DEC 2000

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	JUDY M. REDDICK DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-4346

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/22220

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

IPC(7) :CO8K 5/05; CO8L 61/32

Form PCT/ISA/210 (extra sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/22220

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 19
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The recited "Optiflo L100 "and "Optiflo H600 " per claim 19 are Tradenames and lack sufficient support and descrption in the specification.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.